

# Light Scattering Characterization of Poly(tetrafluoroethylene-co-perfluoromethyl vinyl ether) Copolymer

S.-Q. ZHOU,<sup>1</sup> Q. WAN, D.-H. LIANG,<sup>1</sup> B. CHU,<sup>1</sup> P. XU,<sup>2</sup> J. LAI<sup>2</sup>

<sup>1</sup> Department of Chemistry, State University of New York at Stony Brook, Long Island, New York 11794-3400

<sup>2</sup> W. L. Gore & Associates, Inc., 2401 Singerly Road, Elkton, Maryland 21921-1220

Received 26 May 1999; accepted 17 June 1999

**ABSTRACT:** Static and dynamic light scattering experiments were performed to characterize the copolymer of tetrafluoroethylene (TFE) and perfluoromethyl vinyl ether (PMVE). Solvents of perfluoro-2-butyltetrahydrofuran (FC-75) and Flutec PP11 (PP11) were used to dissolve the TFE-PMVE copolymer. By taking advantage of the solvent properties of FC-75 and PP11, homogeneous TFE-PMVE copolymer solutions were specially prepared in a FC-75/PP11 mixed solvent. Such prepared solutions could provide a strong enough scattered intensity for light scattering studies. The molecular weight, molecular weight distribution, chain dimensions, and conformation were determined for the TFE-PMVE copolymer in the FC-75/PP11 mixed solvent. A combination of viscosity and molecular weight measurements enabled the calculation of the  $k$  value in the relation of  $\eta_0 = k (M_w)^{3.4}$  and thus the prediction of the molecular weight of a given TFE-PMVE copolymer with the same composition by using only the simpler and more readily available rheological measurements. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 733–739, 2000

**Key words:** perfluoroelastomer; light scattering; molecular weight; molecular weight distribution

## INTRODUCTION

Poly(tetrafluoroethylene)s (PTFEs) such as Teflon<sup>®</sup> have excellent thermal stability, as well as extreme chemical, solvent, and oxidation resistance. However, they show poor melt processability. To improve the melt processability and to maintain those excellent desirable properties of PTFE, many types of TFE-based fluorocopolymers have been developed.<sup>1,2</sup> Among them, copolymers of TFE and perfluoro(alkyl vinyl ethers)

[e.g., poly(TFE-co-perfluoromethyl vinyl ether) (TFE-PMVE)] are an important type of perfluoroelastomers.<sup>3</sup> TFE-PMVE copolymers have low glass transition temperatures (below 0°C) while they still maintain high thermal stability up to 316°C. They are mainly used in sealing applications in hostile environments requiring extreme resistance to oxidation, high temperature, aggressive fluids, and chemicals. They are extensively used in the semiconductor, aerospace, aircraft, automotive, chemical, petroleum, and energy industries.

The molecular characterization of TFE-PMVE copolymers is always of interest. However, it is very difficult to obtain information on the molecular weight and molecular weight distribution by

Correspondence to: B. Chu (bchu@notes.cc.sunysb.edu).  
Contract grant sponsor: U.S. Department of Energy; contract grant number: DEFG1286ER45237.015.  
Contract grant sponsor: Army Research Office; contract grant number: DAAG559710022.

*Journal of Applied Polymer Science*, Vol. 77, 733–739 (2000)  
© 2000 John Wiley & Sons, Inc.

conventional gel permeation chromatography (GPC) because very few solvents are available. Solubility is also very limited even if some solvents can be used. Tuminello<sup>4</sup> reported some special fluorocarbon solvents for dissolving fluoropolymers. High temperature laser light scattering (LLS) was successfully applied to the characterization of PTFEs with relatively low molecular weights.<sup>5,6</sup> A centrifuge ball viscometer was developed,<sup>7</sup> and the viscosity of high molecular weight PTFE melts in the  $10^7$  g/mol range was reported.<sup>8</sup>

In this article we present the LLS characterization of a TFE-PMVE copolymer. A suitable solvent is required that not only dissolves the copolymer but also provides a strong enough scattered intensity from the solution. We tried two perfluoro solvents of Flutec PP11 (PP11, predominantly perfluoroperhydrophenanthrene) and FC-75 (predominantly perfluoro-2-butyltetrahydrofuran) to dissolve the copolymer at high temperatures. PP11 is a relatively good solvent for the copolymer. Unfortunately, the refractive index increment from the copolymer solution in PP11 is extremely small so that only very low scattered light intensity can be detected, even with very high solution concentrations. FC-75 may dissolve the copolymer at high temperatures, but its relatively low boiling temperature of 102°C limits the dissolution temperature of the copolymer. There were always some small swollen copolymer particles stuck on the glass bottle wall, even though the copolymer solution in FC-75 was stirred for a very long period of time at 80°C. We finally prepared the solution in a special way by using a mixed solvent of FC-75/PP11 (see the Experimental section). The apparent molecular weight, molecular weight distribution, and chain conformation of the copolymer in the FC-75/PP11 mixed solvent were determined by LLS.

## EXPERIMENTAL

### Materials

The FC-75 (Lancaster Synthesis Inc.) and PP11 (BNFL Fluorochemicals Ltd.) solvents were used as received. These solvents have boiling points of 102 and 215°C, respectively. The TFE-PMVE copolymer sample was a powder supplied by E. I. Du Pont de Nemours and Co. Inc. Fourier transform IR spectroscopy (FTIR, Bio-Rad FTS 3500ARX) was used to determine the copolymer

composition on about 0.1-mm films pressed at 250°C.<sup>9</sup> The absorption band at  $2354\text{ cm}^{-1}$  was used as an internal thickness standard. The PMVE was determined from the absorption band at  $876\text{ cm}^{-1}$ . The amount of PMVE in the copolymer was determined to be 34.7 wt %.

### Solution Preparation

The TFE-PMVE copolymer was first dissolved at 180°C in PP11 solvent at very high concentrations. After being cooled to room temperature, the FC-75 solvent was added to the concentrated solution. The solution with the mixed solvent of FC-75/PP11 was heated to 80°C and stirred for 4 h until the copolymer solution was completely homogeneous. The resulting solution concentration was  $1.0 \times 10^{-3}$  g/mL, and the FC-75/PP11 mixed solvent had a ratio of 96.0/4.0 wt %. The refractive index and viscosity of such a mixed solvent were measured to be 1.279 and 1.40 cP at 25°C, respectively. The stock solution was further diluted to a series of solutions at different desired concentrations by using the FC-75/PP11 mixed solvent having the same composition of 96.0/4.0 wt % at room temperature. Four solutions at concentrations of  $2.1 \times 10^{-4}$ ,  $3.0 \times 10^{-4}$ ,  $4.2 \times 10^{-4}$ , and  $6.7 \times 10^{-4}$  g/mL were obtained. These solutions were clarified by using 1.0- $\mu\text{m}$  Millipore Non-Sterile filters to remove dust.

### LLS Measurements

A standard laboratory-built LLS spectrometer equipped with a BI-9000 AT digital correlator (Brookhaven Instrument Inc.) and a solid-state laser (DPSS, Coherent, 200 mW, 532 nm) was used to perform LLS studies at a scattering angular range of 20–120°. The scattering cell was held in a brass thermostat block filled with a refractive index matching silicone oil. The temperature was controlled to within  $\pm 0.05^\circ\text{C}$ . The differential refractive index increment ( $dn/dC$ ) value of the copolymer solution in the FC-75/PP11 (96.0/4.0 wt %) mixed solvent was measured by using a Brice-Phoenix differential refractometer (model Bp-2000-V) at a wavelength of 546 nm and a temperature of 25°C.

### Dynamic Rheological Measurements

Dynamic rheological measurements were performed by using a Rheometric Scientific ARES rheometer in the frequency-temperature sweep mode. The TFE-PMVE copolymer powder was

first compression molded into a 25.4-mm diameter disk of 1.0-mm thickness at 270°C by using a Carver press. The sample disk was then placed between two 25-mm diameter parallel plates and heated to 250° under dry nitrogen gas in the rheometer. Dynamic mechanical properties were measured at frequencies from 0.1 to 100 rad/s and temperatures from 250 to 325°C with an increment of 25°C. The sample was allowed to equilibrate for a long enough time at each temperature before measurements. The employed strain was sufficiently small to ensure that the measurements were made in the linear viscoelastic regime.

## RESULTS AND DISCUSSION

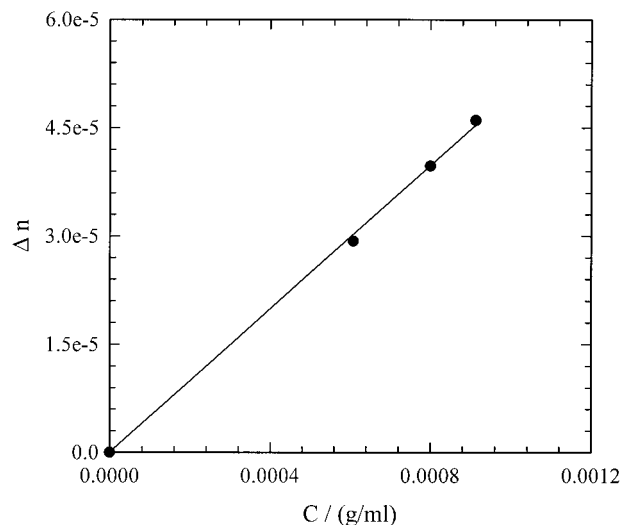
The scattered light intensity of a polymer solution is proportional to the  $(dn/dC)^2$ . It is known that the difference in the refractive index between the fluoro-containing polymer and the perfluorocarbon solvent is relatively small. Thus, an accurate measurement of a small  $dn/dC$  value of TFE-PMVE copolymer in the FC-75/PP11 (96.0/4.0 wt %) mixed solvent is very important to achieve the desired precision in the static LLS results. Figure 1 shows a plot of the differential refractive index  $\Delta n$  ( $n_{\text{solution}} - n_{\text{solvent}}$ ) versus the solution concentration  $C$  for the TFE-PMVE copolymer in the FC-75/PP11 (96.0/4.0 wt %) mixed solvent obtained at a wavelength of 546 nm and a temperature of 25°C. The good linear relation of  $\Delta n$  versus  $C$  gave us a reliable slope value that yielded a  $dn/dC$  value of  $0.0497 \pm 0.0008$  mL/g. Such a  $dn/dC$  value is relatively small, but it is large enough to provide sufficient scattered intensity for LLS characterizations of polymer solutions within an appropriate concentration range.

### Static LLS Measurements

The angular dependence of the excess absolute time-averaged scattered intensity, known as the excess Rayleigh ratio  $R_{vv}(q)$ , was measured. For a dilute solution the  $R_{vv}(q)$  can be expressed as

$$\frac{KC}{R_{vv}(q)} \approx \frac{1}{M_w} \left( 1 + \frac{1}{3} \langle R_g^2 \rangle q^2 \right) + 2A_2 C \quad (1)$$

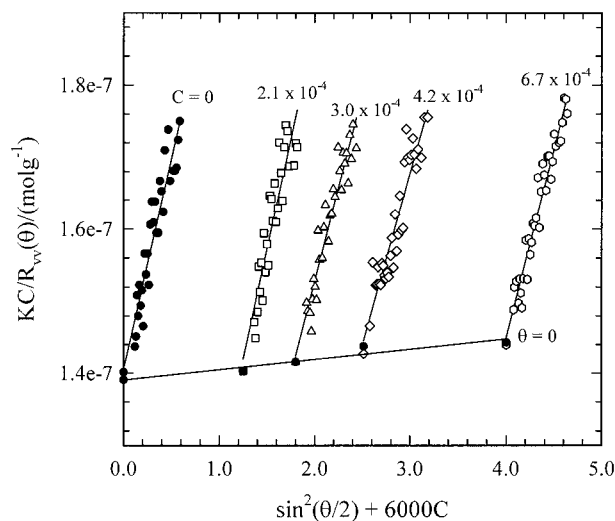
where  $K = 4\pi^2 n^2 (dn/dC)^2 / (N_A \lambda^4)$  and  $q = (4\pi n / \lambda) \sin(\theta/2)$  with  $n$ ,  $dn/dC$ ,  $N_A$ ,  $\lambda$ , and  $\theta$  being the solvent refractive index, the specific refractive in-



**Figure 1** The plot of the differential refractive index  $\Delta n$  ( $n_{\text{solution}} - n_{\text{solvent}}$ ) versus the solution concentration of the TFE-PMVE copolymer in the FC-75/PP11 (96.0/4.0 wt %) mixed solvent obtained at  $\lambda = 546$  nm and  $T = 25^\circ\text{C}$ .

dex increment, Avogadro's number, the wavelength of the incident light *in vacuo*, and the scattering angle, respectively. By measuring  $R_{vv}(\theta)$  over a set of  $C$  and  $\theta$ , we can determine the weight averaged molar mass  $M_w$ , the root mean square radius of gyration  $(R_g^2)^{1/2}$  (written as  $R_g$ ), and the second virial coefficient  $A_2$  from a Zimm plot that incorporates the  $C$  and  $\theta$  dependence of  $KC/R_{vv}(\theta)$  in a single grid. For large particles the linear relation can only be suitable within  $qR_g < 1$ , so the extrapolation must be limited in a low scattering angle region.

Figure 2 shows the Zimm plot of the TFE-PMVE copolymer in the FC-75/PP11 (96.0/4.0 wt %) mixed solvent obtained in a scattering angle range of 20–110° and at concentrations of  $2.1 \times 10^{-4}$  to  $6.7 \times 10^{-4}$  g/mL at 25°C. The  $KC/R_{vv}(\theta)$  depended linearly on both  $\sin^2(\theta/2)$  and  $C$ . The determined  $M_w$ ,  $R_g$ , and  $A_2$  values from the extrapolation of  $[KC/R_{vv}(\theta)]_{\theta \rightarrow 0, C \rightarrow 0}$ ,  $[KC/R_{vv}(\theta)]_{C \rightarrow 0}$  versus  $\sin^2(\theta/2)$ , and  $[KC/R_{vv}(\theta)]_{\theta \rightarrow 0}$  versus  $C$  were  $7.1 \pm 0.4 \times 10^6$  g/mol,  $37.6 \pm 2.5$  nm, and  $4.3 \pm 2.0 \times 10^{-6}$  g<sup>-2</sup> mol mL, respectively. With  $R_g = 37.6$  nm,  $qR_g < 1$  was satisfied in the used scattering angle region of 20–110°. It should be mentioned that for copolymer solutions the determined  $M_w$  is an apparent value due to the composition heterogeneity of the copolymer. However, for the TFE-PMVE copolymer the components of TFE and PMVE have a similar refractive index



**Figure 2** The Zimm plot of the TFE-PMVE copolymer in the FC-75/PP11 (96.0/4.0 wt %) mixed solvent where  $T = 25^\circ\text{C}$  and  $C$  ranges from  $2.1 \times 10^{-4}$  to  $6.7 \times 10^{-4}$  g/mL.

(e.g.,  $n_{\text{PTFE}} = 1.37$  and  $n_{\text{TFE-PMVE copolymer}} \sim 1.35$ , respectively) at  $25^\circ\text{C}$ .<sup>10</sup> The mixed solvent effect can also be neglected in the measurements because PP11 and FC-75 are both perfluoro solvents and only 4.0 wt % PP11 was used in the mixed solvent. The refractive index of the mixed solvent is very close to that of pure FC-75 as measured values of  $n_{\text{FC-75}} = 1.276$  and  $n_{\text{mixed solvent}} = 1.279$ , respectively, at  $25^\circ\text{C}$ . Thus, the determined  $M_w$  value of  $7.1 \times 10^6$  g/mol should be close to the actual molecular weight of the copolymer.

### Dynamic LLS Measurements

The intensity–intensity time correlation function  $G^{(2)}(t, q)$  in the self-beating mode was measured. The  $G^{(2)}(t, q)$  can be related to the electric field time correlation function  $g^{(1)}(t, q)$  as

$$G^{(2)}(t, q) = A[1 + \beta|g^{(1)}(t, q)|^2] \quad (2)$$

where  $A$  is the baseline,  $\beta$  is a parameter depending on the coherence of the detection, and  $t$  is the delay time. The  $g^{(1)}(t, q)$  is further related to the characteristic line width ( $\Gamma$ ) distribution  $G(\Gamma)$  by

$$g^{(1)}(t, q) = \int_0^\infty G(\Gamma)e^{-\Gamma t} d\Gamma \quad (3)$$

The function of  $g^{(1)}(t, q)$  can be analyzed by using a cumulants method<sup>11,12</sup> to obtain the average  $\Gamma$  and the standard deviation for a polydispersed polymer.

$$\ln[g^{(1)}(t, q)] = -\langle\Gamma\rangle t + [1/(2!)]\mu_2 t^2 - [1/(3!)]\mu_3 t^3 + \dots \quad (4)$$

where

$$\langle\Gamma\rangle = \int_0^\infty \Gamma G(\Gamma) d\Gamma \quad \text{and}$$

$$\mu_2 = \int_0^\infty (\Gamma - \langle\Gamma\rangle)^2 G(\Gamma) d\Gamma$$

The value of  $\mu_2/\langle\Gamma\rangle^2$  reflects the polydispersity of detected particles. The molecular weight distribution index can be estimated by using  $M_z/M_w \approx (1 + 4\mu_2/\langle\Gamma\rangle^2)$ .

The  $G(\Gamma)$  can also be calculated from a Laplace inversion of  $G^{(2)}(t, q)$  by a CONTIN program.<sup>13</sup> If the relaxation is diffusive,  $\Gamma$  can be related to the translational diffusion coefficient  $D$  as

$$\Gamma/q^2 = D(1 + k_d C)(1 + f\langle R_g^2 \rangle q^2) \quad (5)$$

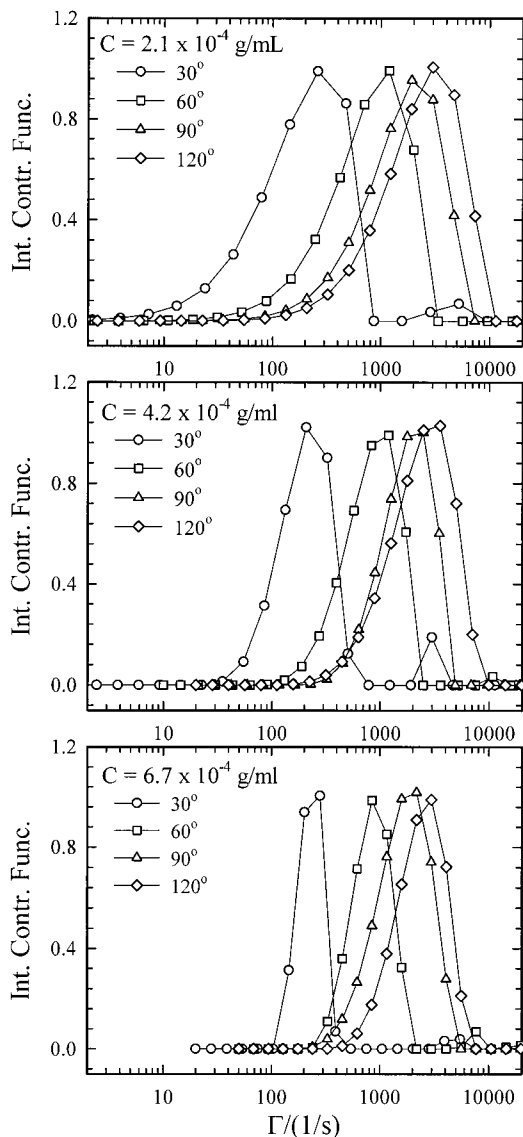
where  $k_d$  is the diffusive second virial coefficient and  $f$  is a dimensionless number related to hydrodynamic draining, internal motion, polydispersity, and solvent quality.<sup>14</sup> After knowing the  $D$  value, the hydrodynamic radius  $R_h$  can be obtained by the Stokes–Einstein equation

$$R_h = k_B T / 6\pi\eta D \quad (6)$$

with  $T$ ,  $k_B$ , and  $\eta$  being the absolute temperature, the Boltzmann constant, and the solvent viscosity, respectively.

Figure 3 shows the angular dependence of the measured characteristic line-width distributions  $G(\Gamma)$ s of the TFE-PMVE copolymer in the FC-75/PP11 (96.0/4.0 wt %) mixed solvent at  $25^\circ\text{C}$  and three different concentrations of  $2.1 \times 10^{-4}$ ,  $4.2 \times 10^{-4}$ , and  $6.7 \times 10^{-4}$  g/mL, respectively. The variance in the line-width distributions ( $\mu_2/\langle\Gamma\rangle^2$ ) did not show an apparent angular dependence. However, the dilution of the solutions led to a broadening of the line-width distribution. The  $\mu_2/\langle\Gamma\rangle^2$  values were determined to be about 0.45,





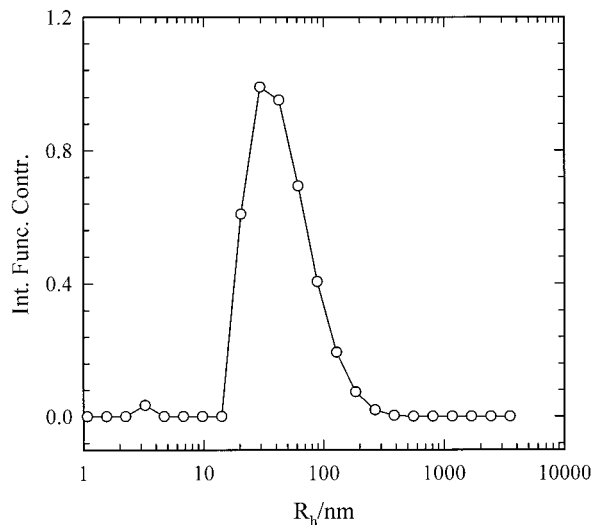
**Figure 3** The angular dependence of characteristic line-width distributions  $G(\Gamma)$  of the TFE-PMVE copolymer in the FC-75/PP11 (96.0/4.0 wt %) mixed solvent at  $T = 25^\circ\text{C}$  and concentrations of  $2.1 \times 10^{-4}$ ,  $4.2 \times 10^{-4}$ , and  $6.7 \times 10^{-4}$  g/mL, respectively.

0.22, and 0.15 for solutions with concentrations of  $2.1 \times 10^{-4}$ ,  $4.2 \times 10^{-4}$ , and  $6.7 \times 10^{-4}$  g/mL, respectively. It could be found that all the four distribution peaks were not symmetric at  $C = 2.1 \times 10^{-4}$  g/mL: a long tail of each distribution curve showed up at the small  $\Gamma$  value side (corresponding to a large particle size). Therefore, the large  $\mu_2/\langle\Gamma\rangle^2$  value at the most dilute concentration of  $2.1 \times 10^{-4}$  g/mL could be partially attributed to the presence of a small amount of dust. By using the  $\mu_2/\langle\Gamma\rangle^2$  values of 0.15–0.22, the index of the

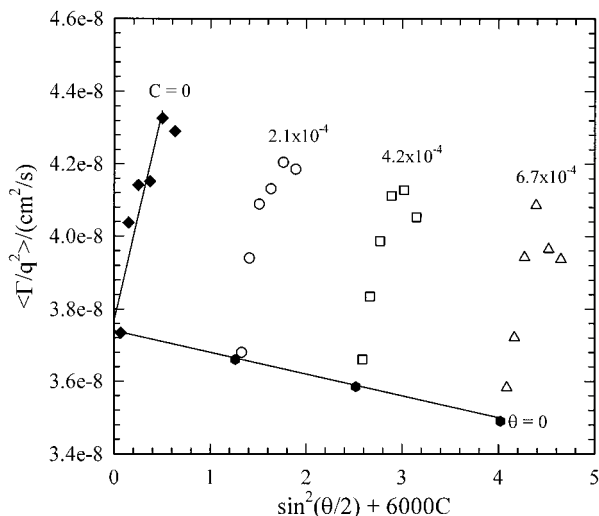
molecular weight distribution ( $M_z/M_w$ ) could be estimated to be about 1.6–1.9 by using  $M_z/M_w \approx (1 + 4\mu_2/\langle\Gamma\rangle^2)$ . Such a polydisperse index value means that the synthetic TFE-PMVE copolymer has a relatively narrow molecular weight distribution.

On the basis of eq. (5) the line-width distributions  $G(\Gamma)$  can be transferred to apparent translational diffusion coefficient distributions  $G(\Gamma/q^2)$ . From the Stokes–Einstein equation the  $G(\Gamma/q^2)$  can be further transferred to a hydrodynamic radius distribution of  $G(R_h)$ . Figure 4 shows a typical hydrodynamic radius distribution of the TFE-PMVE copolymer in the FC-75/PP11 (96.0/4.0 wt %) mixed solvent obtained at  $C = 4.2 \times 10^{-4}$  g/mL,  $\theta = 60^\circ$ , and  $T = 25^\circ\text{C}$ . However, to eliminate the interaction of the copolymer chains in solution, an extrapolation to  $C \rightarrow 0$  and  $\theta \rightarrow 0$  is necessary.

With line-width distributions  $G(\Gamma/q^2)$  obtained at different concentrations and scattering angles, we could calculate the average translational diffusion coefficient  $\langle\Gamma/q^2\rangle$ . Figure 5 shows the dynamic Zimm plot of  $\langle\Gamma/q^2\rangle$  values versus  $[\sin^2(\theta/2) + 6000C]$  for the TFE-PMVE copolymer in the FC-75/PP11 (96.0/4.0 wt %) mixed solvent in the  $\theta$  range of  $30$ – $105^\circ$  and the  $C$  range of  $2.1 \times 10^{-4}$  to  $6.7 \times 10^{-4}$  g/mL at  $25^\circ\text{C}$ . At low  $\theta$  values (e.g.,  $\theta \leq 75^\circ$ ) the  $\langle\Gamma/q^2\rangle$  values showed an angular dependence, while at a high  $\theta$  region the angular dependence of  $\langle\Gamma/q^2\rangle$  could be neglected. In this



**Figure 4** The typical apparent hydrodynamic radius distribution of the TFE-PMVE copolymer in the FC-75/PP11 (96.0/4.0 wt %) mixed solvent obtained at  $C = 4.2 \times 10^{-4}$  g/mL,  $T = 25^\circ\text{C}$ , and  $\theta = 60^\circ$ .



**Figure 5** The dynamic Zimm plot of  $\langle \Gamma/q^2 \rangle$  versus  $[\sin^2(\theta/2) + 6000C]$  for the TFE-PMVE copolymer in the FC-75/PP11 (96.0/4.0 wt %) mixed solvent where  $T = 25^\circ\text{C}$  and  $C$  ranges from  $2.1 \times 10^{-4}$  to  $6.7 \times 10^{-4}$  g/mL.

study the angular extrapolations of  $\langle \Gamma/q^2 \rangle$  to  $\theta \rightarrow 0$  were limited to  $\theta = 30\text{--}75^\circ$ . A combination of extrapolations of  $\langle \Gamma/q^2 \rangle_{\theta \rightarrow 0, C \rightarrow 0}$  led to a  $D$  value of  $(3.75 \pm 0.50) \times 10^{-8}$  cm<sup>2</sup>/s. The corresponding hydrodynamic radius  $R_h$  of the copolymer in FC-75/PP11 (96.0/4.0 wt %) mixed solvent was  $41.3 \pm 4.0$  nm at  $\theta \rightarrow 0$ ,  $C \rightarrow 0$ , and  $T = 25^\circ\text{C}$ . Furthermore, by using eq. (5) the slopes of  $\langle \Gamma/q^2 \rangle_{\theta \rightarrow 0}$  versus  $C$  and  $\langle \Gamma/q^2 \rangle_{C \rightarrow 0}$  versus  $\sin^2(\theta/2)$  could give us a  $k_d$  value of  $-96$  mL/g and an  $f$  value of 0.24. The parameter  $k_d$  is related to the thermodynamic interaction with the equation

$$k_d = 2A_2M_w - k_f - 2\nu \quad (7)$$

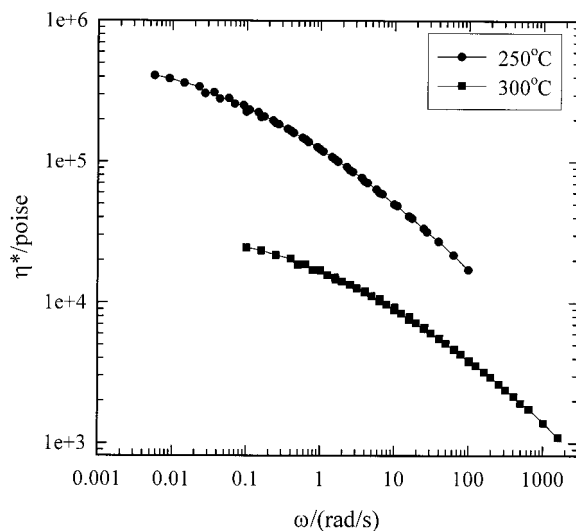
where  $2A_2M_w$  represents the thermodynamic interaction term,  $k_f$  represents the hydrodynamic interaction term, and the  $2\nu$  term ( $\nu$  is the partial specific volume of solvated polymer chains) corrects for the solvent backflow. For a dilute solution the value of  $\nu$  would be small and negligible. Thus, a  $k_f$  value of 157 mL/g was obtained, which implied a substantial attractive hydrodynamic interaction for the TFE-PMVE copolymer chains in the FC-75/PP11 (96.0/4.0 wt %) mixed solvent at  $25^\circ\text{C}$ .

After obtaining the  $R_g$  and  $R_h$  values from static and dynamic LLS, a value of 0.89 for the ratio of  $R_g/R_h$  was found. This value is only slightly larger than the value of 0.77 for a hard

sphere with uniform density, suggesting that the TFE-PMVE copolymer chains exhibited a relatively compact conformation in the FC-75/PP11 (96.0/4.0 wt %) mixed solvent at  $25^\circ\text{C}$ . The TFE-PMVE copolymer was a random copolymer with two components of TFE and PMVE segments on the chains. The FC-75 solvent is selectively a good solvent for PMVE segments, but it is not a good solvent for TFE segments. Therefore, it was possible for the TFE segments to relatively contract while the PMVE segments were relatively extended toward the solvent. Small globules of associated or crumpled TFE segments could be surrounded by the soluble PMVE segments, resulting in a small  $R_g/R_h$  ratio when compared with the value of  $\sim 1.5$  for a Gaussian coil chain.

### Rheological Measurements

The data of complex viscosity ( $\eta^*$ ) versus frequency ( $\omega$ ) at different temperatures were superimposed using the <sup>RSI</sup>Orchestrator time-temperature superposition software (Rheometric Scientific Inc.). A reference temperature of  $300^\circ\text{C}$  was used to construct the master curve using shift factors derived from the Williams-Landel-Ferry equation. Figure 6 shows the complex viscosity as a function of frequency at 250 and  $300^\circ\text{C}$ . The zero-shear viscosity was estimated by fitting the complex viscosity data to the Carreau viscosity model:



**Figure 6** Plots of the complex viscosity  $\eta^*$  of the TFE-PMVE copolymer versus frequency  $\omega$  obtained at  $T = 250$  and  $300^\circ\text{C}$ , respectively.

$$\eta^* = \eta_0 [1 + (A\omega)^C]^{(B-1)/C} \quad (8)$$

where  $A$ ,  $B$ , and  $C$  are fitting constants and  $\eta_0$  corresponds to the zero-shear viscosity. The values of the zero-shear viscosity at 250 and 300°C were  $7.1 \times 10^5$  and  $3.8 \times 10^4$  P, respectively.

The empirical equation of the zero-shear viscosity with the weight average molecular weight could be given by<sup>15</sup>

$$\eta_0 = k(M_w)^{3.4} \quad (9)$$

where  $k$  is a constant that depends on the temperature and polymer composition. With the  $M_w$  value from LLS measurements the values of  $k$  can be calculated by using eq. (9). The obtained  $k$  values were  $1.1 \times 10^{-18}$  and  $6.0 \times 10^{-20}$  at 250 and 300°C, respectively. With an appropriate  $k$  value the  $M_w$  can be easily predicted for a copolymer with the same composition through rheological measurements.

## CONCLUSIONS

The TFE-PMVE copolymer containing 34.7 wt % PMVE can be dissolved in a mixed solvent of FC-75/PP11 (96.0/4.0 wt %) by using a special solution preparation method. LLS can be successfully used to characterize the TFE-PMVE copolymer because the solutions prepared by our method provide a strong enough scattered intensity. The studied TFE-PMVE copolymer has a molecular weight of  $7.1 \times 10^6$  g/mL and a molecular weight distribution of  $M_z/M_w$  of  $\sim 1.6$ – $1.9$ . At 25°C the TFE-PMVE copolymer chains have substantial attractive hydrodynamic interactions and show a compacted globule conformation in

the FC-75/PP11 (96.0/4.0 wt %) mixed solvent. By using an empirical equation of  $\eta_0 = k(M_w)^{3.4}$ , the combination of light scattering and rheological measurements enabled us to predict the molecular weight information for a given copolymer with the same composition.

## REFERENCES

1. Yamabe, M. *Prog Pacific Polym Sci* 1991, 67.
2. Uschold, R. E. *Polym J* 1985, 17, 253.
3. Logothetis, A. L. *Prog Polym Sci* 1989, 14, 251.
4. Tuminello, W. H. In *Proceedings of the 3rd Conference in the Series: High Performance Coating Materials—Fluorine in Coatings II*, February 24–26, 1997, Munich, Germany.
5. Chu, B.; Wu, C.; Buck, W. *Macromolecules* 1988, 21, 397.
6. Chu, B.; Wu, C.; Buck, W. *Macromolecules* 1989, 22, 831.
7. Linliu, K.; Yeh, F.; Shook, J. W.; Tuminello, W. H.; Chu, B. *Rev Sci Instrum* 1994, 65, 3823.
8. Chu, B.; Linliu, K. *Macromolecules* 1995, 28, 2723.
9. Aten, R. M.; Jones, C. W.; Olson, A. H. *World Pat. C08F 214/26* (1997).
10. Brandrup, J.; Immergut, E. H., Eds. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989; Vol. 35.
11. Koppel, D. E. *J Chem Phys* 1972, 57, 4814.
12. Chu, B.; Ford, J. R.; Dhadwal, H. S. In *Methods of Enzymology*; S., Colowick, N. O., Kaplan, Eds.; Academic: Orlando, FL, 1985; Vol. 117.
13. Provencher, S. W. *Makromol Chem* 1979, 180, 201.
14. Burchard, B.; Schmidt, M.; Stockmayer, W. H. *Macromolecules* 1980, 13, 580.
15. Graessley, W. W. In *Physical Properties of Polymers*, 2nd ed.; J. E., Mark, A., Eisenberg, W. W., Graessley, L., Mandelkern, E. T., Samulski, J. L., Koenig, G. D. Wignall, Eds.; American Chemical Society: Washington, D.C., 1993.